

Orbital Order, Stripe Phases and Mott Transition in a Planar Model for Manganites

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Understanding orbital ordered (OO) Mott insulating states lies at the heart of a consistent resolution of the colossal magneto-resistance (CMR) observed in manganites, where its melting induces a low- T insulator-metal transition for $0.25 \leq x \leq 0.45$. Motivated thereby, we study the OO states in a planar model for bilayer manganites using DMFT and finite-size diagonalisation methods. We derive the correct OO ground states observed in manganites for $x = 0, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}$ in exact agreement with observations, including the charge-orbital-magnetic ordered stripe phases for $x > \frac{1}{2}$. These OO states are *exactly* shown to be associated with an “alloy” ordering of the $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbitals on each Mn^{3+} site.

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Colossal magnetoresistance (CMR) materials have received much attention [1, 2], due to their extreme sensitivity to minute perturbations [3]. The parent (cubic perovskite) materials are Mott-Hubbard insulators with G -type (AF) orbital order of $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbitals and A -type AF spin order [3]. Upon hole doping, x (divalent ion substitution) in $La_{1-x}Ca_xMnO_3$, for example, they evolve through ferromagnetic, orbital ordered (OO) Mott insulators with unusual properties [4], to a ferromagnetic metal (FM) at low- T . A transition to a paramagnetic insulator (PI), dependent upon cation-dopant type, is seen for $T > T_c$ [3]. A small magnetic field suppresses this I-M transition, leading to CMR. These phenomena are also seen in bilayer manganites. Further, more “strange” OO states are found in “overdoped” (with Ca) manganites. The half-doped manganites show a charge (C), orbital and AF order that is very sensitive to small perturbations [5] ($H_{ext} = 5 - 7$ T gives a ferromagnetic metal with no CO/OO). The “overdoped” manganites with $x = \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, \frac{4}{5}$ show extremely stable pairs of $Mn^{3+}O_6$ Jahn-Teller distorted stripes having periods between $2 - 5a$ (a =unit cell length); for other values of x , a mixture of the two adjacent commensurate configurations is found [6]. For $x = 1$, $CaMnO_3$ is again an AF ($S = \frac{3}{2}, t_{2g}$) Mott insulator. Finally, the correlated nature of manganites is shown by dynamical spectral weight transfer (SWT) over large energy scales $O(4.0$ eV) in various [7, 8, 9] studies as a function of x, T, B_{ext} -this can only result from strong electronic correlations. The importance of the Jahn-Teller (JT) coupling is evidenced by the large isotope effects [10] and by I-M transitions driven by $O^{18} \rightarrow O^{16}$ isotope substitution [11] (see, however, Ref. [12], where the JT coupling is argued to be much weaker than in [10, 11]). Thus, understanding CMR is inextricably linked to understanding how these strongly coupled orbital-spin-charge correlations are modified by small perturbations as a function of x . A unified description of these unusual observations in one picture is a formidable challenge for theory.

The CMR problem has been extensively tackled in literature [13, 14] using a variety of numerical and analytic (QMC and $D = \infty$) methods, for double exchange (DE) models, with/without Jahn-Teller phonons, as well as with strong multi-orbital Coulomb interactions with static/dynamic JT phonons [14]. For OO states, the full multi-orbital Hubbard model has been studied by mapping it to a Kugel-Khomskii (KK) model [15]. However, a controlled treatment (semiclassical analysis [16] indicates an order-by-disorder mechanism) is hard: even the type of order is unclear there, and the results sensitively depend on the approximations used [17].

Here, we take the first step to study the OO, Mott insulating phases observed in CMR manganites within a 2D, multi-orbital Hubbard model incorporating the above-mentioned strongly coupled correlations. Our conclusions apply, with small additional modifications (to be treated separately) to bilayer manganites. We show that a 2D model suffices to capture the correct OO states observed as a function of doping, x , and leave the full 3D problem for a separate work. Going beyond previous studies [14, 17], we show how incorporation of the realistic structure of a single MnO_4 layer explicitly in the one-electron hopping integrals introduces new, unanticipated features, making a qualitative difference to the physical results for all x . Further, we show how the “strange” stripe-ordered phases in the global phase diagram are naturally rationalised from our effective model.

We start with a model that explicitly includes orbital degeneracy of the e_g orbitals in manganites [2],

$$\begin{aligned}
 H = & - \sum_{\langle ij \rangle, a, b} t_{ij}^{ab} (a_{i\sigma}^\dagger b_{j\sigma} + h.c.) + U \sum_{i, \beta=a, b} n_{i\beta\uparrow} n_{i\beta\downarrow} \\
 & + U' \sum_{i\sigma\sigma'} n_{ia\sigma} n_{ib\sigma'} - J_H \sum_{i\sigma\sigma'} \mathbf{S}_i \cdot \sigma_i (a_{i\sigma}^\dagger a_{i\sigma'} + b_{i\sigma}^\dagger b_{i\sigma'}) \\
 & + H_{JT}, \tag{1}
 \end{aligned}$$

where the a and b are fermion annihilation operators in the doubly degenerate e_g orbitals, t_{ij}^{ab} ($a, b =$

$d_{3x^2-r^2}, d_{3y^2-r^2}$) is a 2×2 matrix in orbital space incorporating realistic features of the basic $Mn-O$ perovskite structure [18]. U, U' are the on-site, intra- and inter-orbital Hubbard interactions, and J_H is the (strong) Hund's rule coupling giving rise to the FM state as in the usual DE model. Polaronic effects are described by H_{JT} (see below).

At strong coupling, setting $U, J_H \gg t$ gives the following effective Hamiltonian, $H_0 = -\sum_{ij,a,b,\mu} t_{ij}^{ab} \gamma_{ij}(\mathbf{S})(a_i^\dagger b_j + h.c)$ with $\mu = x, y$. Here, $t_x^{ab} = \frac{t}{4}[3, \sqrt{3}, \sqrt{3}, 1]$ and $t_y^{ab} = \frac{t}{4}[3, -\sqrt{3}, -\sqrt{3}, 1]$ define the one-electron hopping matrix for a single manganite layer. We now turn on U' . One is effectively dealing with spinless fermions, but now with an orbital index. Clearly, this model ($U' = 0$) cannot access the interplay between magnetism and OO in manganites. With U' and the JT coupling terms, H becomes

$$H_{eff} = H_0 + U' \sum_{i,a \neq b} n_{ia} n_{ib} + H_{JT}, \quad (2)$$

where $\gamma_{ij}(\mathbf{S})$ is the usual DE projection factor [3].

Transform to new variables, $c_{\alpha\uparrow} = (a + (-1)^\alpha \sqrt{3}b)/\sqrt{2}$, $c_{\alpha\downarrow} = ((-1)^\alpha \sqrt{3}a - b)/\sqrt{2}$ with $(-1)^\alpha \equiv +1$ ($\alpha||x$) and $\equiv -1$ ($\alpha||y$). The $c_{\alpha\sigma}$ transform exactly like $d_{3x^2-r^2}(\uparrow)$, $d_{3y^2-r^2}(\downarrow)$. This *exactly* yields a Falicov-Kimball model (FKM) where only the $c_{\alpha\uparrow}$ hop; the $c_{\alpha\downarrow}$ are strictly immobile as long as no JT distortions are included. Thus,

$$H_{eff} = - \sum_{\langle ij \rangle, \alpha} t \gamma_{ij}(\mathbf{S})(c_{i\alpha\uparrow}^\dagger c_{j\alpha\uparrow} + h.c) + U' \sum_{i,\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + H_{JT} \equiv H_{FKM} + H_{JT}, \quad (3)$$

reflecting the correlation between the magnetic and orbital degrees of freedom described above.

In orbital space, the JT coupling corresponds to addition of external fields [18], $H_{JT} = Q_2 \sum_i (n_{ia} - n_{ib}) + Q_3 \sum_i (a_i^\dagger b_i + h.c)$. In the rotated basis, this is,

$$H_{JT} = Q_{++} \sum_{i,\alpha} (n_{i\alpha\uparrow} - n_{i\alpha\downarrow}) + Q_{+-} \sum_{i,\alpha} (c_{i\alpha\uparrow}^\dagger c_{i\alpha\downarrow} + h.c), \quad (4)$$

where $Q_{++} = ((-1)^\alpha \sqrt{3}Q_2 - Q_3)/2$ and $Q_{+-} = (Q_2 + (-1)^\alpha \sqrt{3}Q_3)/2$ are staggered JT distortions which follow the orbital (electronic) variables. So $H_{eff} = H_{FKM} + H_{JT}$ is a FKM with a local, staggered hybridisation between the $c_{\alpha\uparrow}, c_{\alpha\downarrow}$ at each site. Inclusion of finite phonon frequency ($M\Omega^2(Q_2^2 + Q_3^2)/2$) and intersite phonon coupling terms is required in a full analysis: we have not done this here.

For a half-filled band of spinless fermions, the exact solution of H in $D = 2$ implies an anti-ferro orbital order of $d_{3x^2-r^2}, d_{3y^2-r^2}$, exactly as required [19]. Such a FKM has been employed earlier [14, 17] for manganites,

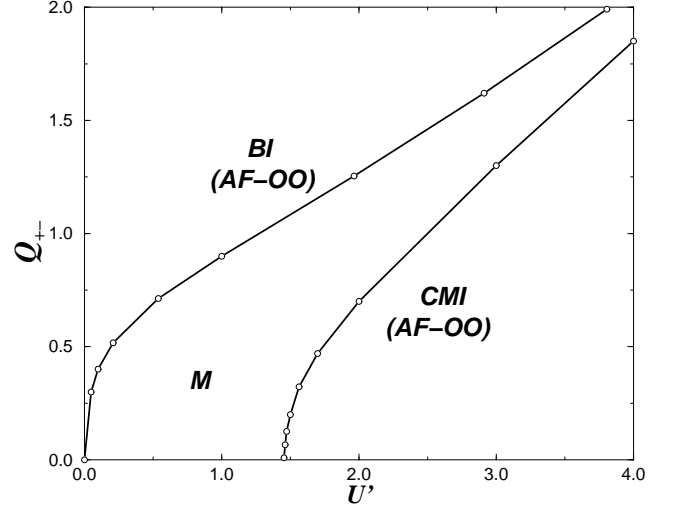


FIG. 1: Phase diagram for the transformed multi-orbital model with $Q_{++} = 0$ at half-filling. The charge Mott (CMI) and the band (BI) insulators, both with anti-ferro-orbital order (AF-OO) are separated by an incoherent, pseudogapped metal (M) phase.

but $c_{\alpha\uparrow} = d_{x^2-y^2}, c_{\alpha\downarrow} = d_{3z^2-r^2}$ there. This would lead to an AFOO of $d_{x^2-y^2}/d_{3z^2-r^2}$, at variance with observations. Here, such a FKM follows *exactly* from the realistic hopping structure. Moreover, the AF-OO (Mott insulating, see below) state is driven by large U' , in contrast with band-based scenarios. We note that Yamasaki *et al.* [20] have derived an AF-OO Mott insulator for cubic LaMnO_3 (with $x = 0$) using LDA+DMFT. Our work is thus complementary to theirs for $x = 0$, but goes much further, permitting us to study the “exotic” OO states for $x \geq \frac{1}{2}$ as well (see below). Moreover, given our effective FK mapping [21], the OO state(s) are readily understood in terms of an “alloy” ordering of $d_{3x^2-r^2}, d_{3y^2-r^2}$ orbitals at *each* Mn site.

We now solve $H_{eff} = H_{FKM} + H_{JT}$ in $d = \infty$. As shown earlier [19], DMFT works surprisingly well for the 2D FKM. The FKM with/without Q_{+-} has an almost exact solution in $D = \infty$ [22]. The formalism is essentially the same as that used previously, and gives very good agreement with QMC results for the same model [23]. Keeping U'/t fixed and large, phase transitions from the Mott insulator with AF-OO to correlated (incoherent) metal with no OO, to a correlation-assisted band insulator, again with AF-OO, occur: this is indeed borne out in the $D = \infty$ solution, as shown in Fig. 1. Given that U' is much larger than Q_{++}, Q_{+-} in H above, we conclude that manganites fall into the CMI class with AF-OO, and that the JT terms lead to additional stabilization of both. Finally, DMFT gives the full, correlated spectral functions of the model for arbitrary parameter values and band-fillings, at a very modest numerical cost. This allows us to study the filling driven Mott transition

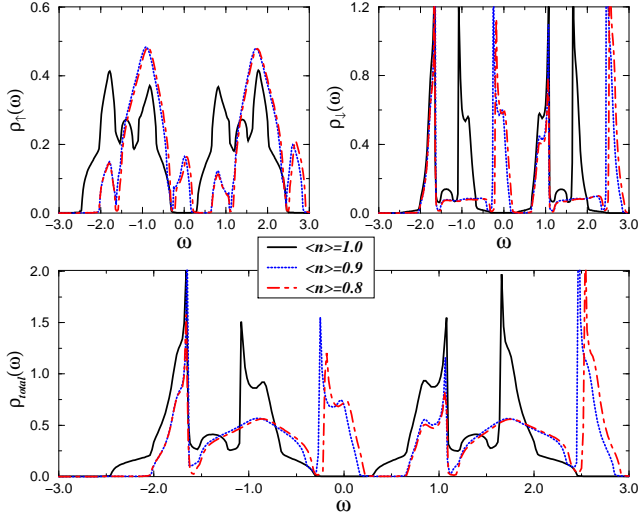


FIG. 2: (Color online) Partial orbital-resolved (top panels) and the total many-body DOS for the AF-OO phase of H_{eff} (see text) within DMFT for $U' = 2.6$ eV, and *staggered* $Q_{++} = 0.3$ eV, $Q_{+-} = 0.4$ eV, for various band-fillings. Off-diagonal components of the spectral function are not shown. For $\langle n \rangle = 0.9, 0.8$, the low-energy pseudogap at $\omega = 0$ is clearly seen in the DOS.

from an AF-OO Mott insulator to an incoherent metal (see below).

The relevant DMFT equations were derived earlier [22], so we do not repeat them here. Since the JT terms are staggered, but bilinear in the e_g basis, they are easily incorporated into the earlier DMFT structure. The Green function is now a (2×2) matrix in orbital space. The staggered, JT “external field” terms imply an averaging over their orientations, which is carried out within the DMFT equations to yield the DOS. We choose $U' = 2.6$ eV, $Q_{++} = 0.3$ eV, $Q_{+-} = 0.4$ eV as model parameters along with a non-interacting DOS for the 2D square lattice with bandwidth, $W = 2.0$ eV and variable band-filling, $n = (1 - x)$, in the DMFT solution. For $n = 1$, (see Fig. 2) we obtain an AFOO Mott insulator. This is obtained from the computed value of $D_{1\alpha} = (-1)^\alpha \langle (c_{i\alpha\uparrow}^\dagger c_{i\alpha\downarrow} + h.c.) \rangle = C(\frac{U'}{W}, Q_{++}, +, -) = 0.07$ and $D_{2\alpha} = (-1)^\alpha \langle (n_{i\alpha\uparrow} - n_{i\alpha\downarrow}) \rangle = C'(\frac{U'}{W}, Q_{++}, +, -) = 0.05$ (not shown), obtained directly from $D_{2\alpha} = -\frac{1}{\pi} \int \sigma \text{Im} G_{\alpha\sigma}(\omega) d\omega$ and $D_{1\alpha} = -\frac{1}{\pi} \int \text{Im} G_{\alpha\uparrow\downarrow}(\omega) d\omega$ from the DMFT equations. Away from $n = 1$, the DMFT equations have to be supplemented with the Friedel-Luttinger sum rule, $\langle n \rangle = -\frac{1}{\pi} \int_{-\infty}^{E_F} \sum_{\alpha, \sigma} \text{Im} G_{\alpha\sigma}(\omega) d\omega$. This is computed self-consistently within the DMFT.

For $\langle n \rangle = 0.9, 0.8$, we obtain an *incoherent*, pseudogapped, metallic state (see Fig. 2) with a sharp reduction of local anti-ferro orbital (AFO) correlations ($D_{1\alpha} = 0.009$). Thus, appearance of the doping-driven

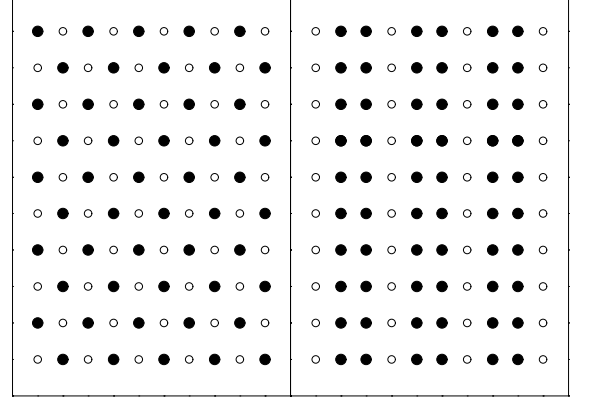


FIG. 3: Two different charge-orbital ordered (COO) ground states of the effective Falicov-Kimball model for $x = \frac{1}{2}$ (left) and $x = \frac{2}{3}$ (right). These exactly correspond to the COO states observed in manganites for these x values [2, 6].

(FM) metallic state is intimately linked to the “melting” of local anti-ferro orbital correlations of the Mott insulator with x . The non-FL character of the FM contrasts with what is expected in the FKM with uniform hybridisation ($V = Q_{+-}$ in the usual FKM with hybridization), where a correlated FL metal is obtained whenever V is relevant [24]. In our model, the staggered “fields” $Q_{++}, +, -$ produce a low-energy pseudogap, suppressing FL coherence. Chemical disorder will further reinforce incoherence [26]. Given the d -wave character of the staggered JT terms (note that both $Q_{++}, +, -$ have components that change sign under a $\pi/2$ rotation in xy plane), as well as the (more important) fact that d -wave ground states are obtained near half-filling in a Hubbard-like (FKM) model [25], we predict that this incoherent FM-metal phase will exhibit a d -wave pseudogap.

In contrast to earlier FKM work [14, 17], however, the ordered, insulating phases in un(doped) manganites arise naturally from our model. The checkerboard order of $d_{3x^2-r^2}, d_{3y^2-r^2}$ corresponds to an AF-OO insulator. The exotic bi-stripe states too are naturally predicted from the analysis of our FKM. In the insulating phases, the “hybridisation” (Q_{+-}) is irrelevant, and the resulting FKM rigorously undergoes phase separation into hole-rich (orbital disordered) and hole-poor (orbitally ordered) phases, as shown by Freericks *et al.* [21] by minimizing the total energy for various x . We have repeated their analysis for various $x \geq 0.5$. For $x = \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, \frac{4}{5}$, we obtain stripe phases with periods 2, 3, 4, 5, as observed by Mori *et al.* [6] using electron diffraction. In Fig. 3, we show only the OO ground states for $x = \frac{1}{2}, \frac{2}{3}$; these exactly correspond to those observed in manganites for

these hole dopings.

Given that $Mn^{3+,4+}$ correspond to one/zero e_g electron on each Mn site, the 2D model automatically has charge order (CO) of the correct types for these values of x . Also, the stripe OO of pairs of $Mn^{3+}O_6$ (distorted) octahedra automatically corresponds to a bi-stripe charge-order (CO) of e_g electrons with the periodicity determined by x [2]. Given the bi-stripe OO states, Goodenough-Kanamori-Anderson rules directly imply that intersite interactions between the “core” t_{2g} spins ($S = 3/2$) will lead to AF-coupled ladders (Mn^{3+}) separated by strips of JT-undistorted (Mn^{4+}) regions. Given suppression of e_g hopping in an AF “background”, these stripe states will be insulators, as observed [1, 2]. These states will be further stabilised upon inclusion of JT terms and longer range elastic interactions.

This fully corresponds to observations in bilayer manganites for $x > 0.5$ [2]. Thus, stripe states in “overdoped” CMR *exactly* result from an “alloy” ordering of a binary alloy of Mn^{3+} ($S = 2, d^4$) and Mn^{4+} ($S = \frac{3}{2}, d^3$) orbitals with $d_{3x^2-r^2}, d_{3y^2-r^2}$ symmetry. Phase separation/stripe phases have long been studied using the FKM (binary alloy disorder model) in alloy physics [27]. Here, we show how these phenomena in manganites arise from strong, multi-orbital, *electronic* correlations, which are now exactly representable as a binary alloy model. Since OO states spontaneously break *discrete*, Ising symmetries of H (Eq. (1)), the link to alloy ordering (described within an Ising model framework [27]) is readily apparent. Recently [28], OO phases in a 3D model were derived within a static Hartree-Fock approximation. In future, we will make contact with these results.

To conclude, we have shown how consideration of the actual multi-orbital structure of the hopping matrix in the e_g sector within a multi-orbital correlated model results in an understanding of the various OO insulating phases observed in CMR manganites, especially in bilayer cases, as a function of x . These are now understood simply as an “alloy” ordering of $d_{3x^2-r^2}, d_{3y^2-r^2}$ orbitals, driven predominantly by the inter-orbital correlations (U'). Our study shows that OO in overdoped ($x > 0.5$) manganites need not imply very strong JT coupling, in agreement with [12]: by itself, U' leads directly to such phases as a function of x . A moderate JT distortion will further stabilise these ordered phases. Within multi-orbital DMFT, we have shown how an AFOO/F Mott insulator turns into a correlated, incoherent, ferromagnetic “bad metal” upon hole doping. This goes hand-in-hand with a drop in local AFO correlations. These results are fully consistent with indications from a host of experiments probing various phases of doped bilayer manganites. Interestingly, planar nickelates are also modelled by a similar Hamiltonian, and our work also naturally explains the OO/stripe phases observed there [29]. We expect our analysis to be broadly applicable to a variety of TMO systems showing a variety of

OO/magnetic ground states as a function of a suitable “tuning parameter”.

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